

International Journal of Chemical and Biochemical Sciences (ISSN 2226-9614)

Journal Home page: www.iscientific.org/Journal.html



© International Scientific Organization

# Corrosion inhibition effects of the essential oils of two Asteraceae plants from South Algeria

Faiza Chaib<sup>1</sup>, Hocine Allali<sup>1</sup>, Omar Benali<sup>2</sup>\* and Guido Flamini<sup>3</sup>

<sup>1</sup>Laboratoire des Substances Naturelles & Bioactives (LASNABIO), Département de Chimie, Faculté des Sciences, Université Abou Bekr Belkaïd, BP 119, Tlemcen 13000, Algérie, <sup>2</sup>Department of Biology, Faculty of Sciences, University Dr Tahar Moulay of Saïda, Algeria and <sup>3</sup>Dipartimento di Farmacia Via Bonanno 6, 56126 Pisa, Italy

# Abstract

The chemical composition and anticorrosion activities of essential oils obtained from two plants growing wild in southern Algeria, *Asteriscus graveolens* (FORSSK.) LESS. and *Pulicariaincisa* (LAM.) DC, have been investigated. Chemical analysis was by GC-MS. The main component of *A. graveolens* were cis-chrysanthenyl acetate (31.1%), myrtenyl acetate (15.1%), and kessane (11.5%), while for *P. incisa* the major ones were chrysanthenone (45.3%) and 2,6-dimethylphenol (12.6%). The hydro-distilled oils obtained from the aerial parts were tested at various concentrations as corrosion inhibitors by means of polarization curves, polarization resistance and electrochemical impedance spectroscopy (EIS). The oils acted as efficient inhibitors against mild steel in 1 M HCl medium, and their inhibition efficiency increased with the inhibitor concentration, reaching a value of upto 82.05% at 0.3 g/L, especially for *P. incisa* that showed the highest anticorrosion effect compared to *A. graveolens*. Polarization study showed that *P. incise* oil was a mixed-type inhibitor and its adsorption on the metal surface follows a Langmuir isotherm. These results give significant information about the anticorrosion activities of these essential oils, which suggest their possible use for industrial purposes.

Keywords: Essential oil, GC-MS; corrosion inhibitor; mild steel; Anticorrosion properties

 Full length article
 \*Corresponding Author, e-mail: benaliomar@hotmail.com, Tel: (+213) 656258886

# 1. Introduction

It is known that the aggregation of an acid on a metal surface causes its dissolution. In the industrial field, acids find several applications (cleaning and acid stripping) with consequent severe corrosion of metals [1-3]. It should also be noted that many acids, such as nitric [4], phosphoric [5], hydrochloric [6-10] and sulfuric [11,12] ones are widely used in this application context. HCl is commonly used in the pickling industry because of its low cost compared to the other acids [13-15]. However, the use of inhibitors in aggressive solutions can reduce the corrosion rate of mild steel. In addition, an inhibitor is said to be effective if there are hetero atoms in its structure. Moreover, the effectiveness of an inhibitor depends on several factors, mainly its chemical structure, the type of metal and the aggressive environment. On the other hand, the high cost and toxicity of organic inhibitors, drive researchers to look for ecological inhibitors and thus, several studies have been conducted on the protection of metals and especially steels against corrosion by the essential oils obtained from plant material [5, 10, 16].

In this study, the essential oils of two plants growing in southern Algeria, in particular Asteriscus graveolens (FORSSK.) LESS. and Pulicar iaincisa (LAM.) DC. were evaluated. No studies have been previously published about the use of the essential oils of these two species as corrosion inhibitors. A. graveolens is a plant of the genus Asteriscus, belonging to the Inula-group of the Asteraceae-Inuleae. A. graveolensis the accepted scientific name of this species and has as synonyms Bubonium graveolens, Odontospermum graveolens and Nauplius graveolens [17, 18]. It is common in the Hoggar located in the province of Tamanrasset (Southern Algeria). Locally, it is known as "Tameyout", and has been used in the folk medicine for treating cephalic pains and fever [19]. P. incisa belongs to the genus Pulicaria, included into the tribe Inuleae of the Asteraceae family. It is frequent in Hoggar and it is also known as P. undulata (L.) DC., P. desertorum DC., and P. prostrata (GILIB.) ASCHERS. It is locally called "Ameyou". In Algeria, its decoction is used against colds, flu and tachycardia [19].

In the current research work, a detailed study on the chemical composition of the hydro-distilled oils of *A. graveolens* and *P. incise* is reported. Moreover, their properties as corrosion inhibitors were assayed for mild steel in 1M HCl medium using as experimental techniques polarization curves, polarization resistance and electrochemical impedance spectroscopy (EIS).

#### 2. Materials and methods

# 2.1. Plant material

Aerial parts of the wild growing *A. graveolens* and *P. incisa* were gathered at the flowering stage in Tamanrasset [Hoggar, South of Algeria, Latitude 22°40'384" S, Longitude 5°31'238" E, Altitude 1266 m] during spring 2014. The species were taxonomically identified by Dr. Rabéa Sahki. A voucher specimen of each species was deposited at the Herbarium of the National Forest Research Institute, Tamanrasset (Algeria), under the registration numbers AGAP 114 and PIAP 111, respectively for *A. graveolens* and *P. incisa*. The plant material were airdried under a laboratory shade and stored for future use.

## 2.2. Isolation of the essential oils

Essential oils were obtained from dried aerial parts of *A. graveolens* and *P. incisa* (500 g of each) by hydrodistillation for 5 h, using a *Clevenger*-type apparatus, according to the method recommended in the *European Pharmacopoeia* [20]. The isolated oils were collected by decantation, dried over anhydrous MgSO<sub>4</sub>, weighted and then stored in sealed glass vials at  $+4^{\circ}$ C for later GC-MS analysis and corrosion tests.

## 2.3. Chemical analysis

The analysis of the essential oils was performed as previously reported [21].

# 2.4. Materials and solution

Corrosion tests were performed on mild steel having the following composition (% by weight): C: 0.14-0.22, Mn: 0.50-0.80, Si: 0.15-0.30, S: 0.05, P: 0.05, Cu: 0.5, Cr: 0.30, Ni: 0.03, Mo: 0.05, V: 0.08, Sn: 0.05 and Fe balance. An aggressive 1M HCl solution was prepared by diluting 37% HCl using distilled water. Before each measurement, the mild steel samples were polished with emery paper (400 to 800 grades), cleaned with acetone and then rinsed with distilled water and dried.

#### 2.5. Electrochemical measurements

Electrochemical impedance spectroscopy (EIS) is an analytical method used to examine the interface system (metal as electrode-solution). The amplitude of the sinusoidal voltage applied to the abundant potential is 10 mV peak-to-peak at frequencies between 100 kHz and 100 mHz. The equivalent electric circuit was determined according the Z-view program. Measurements of EIS and *Chaib et al.*, 2020

potentiodynamic polarization were performed using a PGZ 301 potentiostat piloted with Voltamaster 4. For the electrochemical tests, a three-electrode cell, double-wall thermostat with a capacity of 500mL, were used. The three electrode were: auxiliary electrode in platinum; saturated calomel electrode (SCE) as reference electrode and mild steel used as working electrode (S=0.16 cm<sup>2</sup>). The AC impedance measurements were performed at corrosion potentials (E<sub>corr</sub>) and the Nyquist plots were obtained. Measurements were conducted after maintaining the working electrode at its circuit potential for 30min (favorable time for the potential of the studied system to become stable). The potentiodynamic current-potential curves were recorded by changing the electrode potential automatically from -600 to -200mV at a scanning rate of 30mV/min, under static on the same electrode without any surface treatment. Corrosion current densities were determined by extrapolating the cathodic and anodic Tafel regions from the potentiodynamic polarization curves to the corrosion potential. All the experiments were carried out in freshly prepared solution at constant temperature. The fixed temperature was maintained using a water bath equipped with a thermostat.

## 3. Results and discussions

#### 3.1. Chemical study

The essential oils of the aerial parts of A. graveolens and P. incise were obtained at 0.30 and 0.50 % vields (w/w), respectively. The hydro-distilled oils were yellowish-green and pale yellow, with aromatic, fragrant and pleasant odors. The compositions of the two essential oils are in good agreement with previous studies on the same species growing within the Mediterranean area [12, 22]. The chromatographic profile of the essential oil of the aerial parts of A. graveolens from Algeria, permitted to evidence that it is constituted exclusively by terpenoids. A total of 31 compounds were characterized, representing 97.0% of the total oil: 8 oxygenated monoterpenes (53.9%), 13 oxygenated sesquiterpenes (35.2%), 6 monoterpene hydrocarbons (5.7%) and 4 sesquiterpene hydrocarbons (2.2%). The principal components were *cis*-chrysanthenyl acetate (31.1%), myrtenyl acetate (15.1%), kessane (11.5%), liguloxide (7.4%), *cis*-chrysanthenol (5.3%), T-cadinol (4.5%), and valerianol (3.8%) (Table 1). In the essential oil isolated from the aerial parts of P. incisa, 42 components representing 97.3% of the whole oil were characterized. The oil was mainly composed by terpenoid derivatives, but also non-terpene compounds were identified. The oxygenated terpenoids were found in higher percentages: 13 monoterpenes (55.2%) and 12 sesquiterpenes (18.8%). A small amounts of monoterpene-hydrocarbons accounted for 1.4%, together with 6 sesquiterpene hydrocarbons (4.8%) and 5 non-terpene derivatives (17.1%). The major constituents of the oil were chrysanthenone (45.3%), 2,6dimethylphenol (12.6%),  $\alpha$ -cadinol (5.6%), eudesma-4(15),7-dien-1-ol (3.5%) and T-cadinol (3.6%) (Table1).

# **Table 1:** Chemical compositions of A. graveolens and P. incisa aerial parts essential oils

			Essential Oils (%) <sup>c</sup>			
No. <sup>a</sup>	No. <sup>a</sup> Compounds		А.	<i>P</i> .	Identificat	
	•		graveolens	incisa	ion <sup>d</sup>	
1	α-Pinene	941	2.6	0.2	RI, MS	
2	Sabinene	977	0.2	0.2	RI, MS	
3	Myrcene	993	2.2	-	RI, MS	
4	α-	1006	0.3	-	RI, MS	
	Phellandrene					
5	<i>p</i> -Cymene	1028	0.1	0.3	RI, MS	
6	Limonene	1032	0.3	0.3	RI, MS	
7	cis-	1076	-	0.5	RI, MS	
	Linalooloxid					
	e (furanoid)					
8	Terpinolene	1090	-	0.4	RI, MS	
9	Linalool	1101	0.2	-	RI, MS	
10	2,6-	1105	-	12.6	RI, MS	
	Dimethylphe					
	nol	1105			<b>DI</b> 1 <b>I G</b>	
11	<i>p</i> -	1107	-	2.3	RI, MS	
	Methylbenzy					
10	lalcohol	1106		45.0	DI MG	
12	Chrysanthen	1126	-	45.3	RI, MS	
12	one	1141		0.6	DI MC	
15	Z- Ethylphonol	1141	-	0.0	KI, MS	
1.4	Ethylphenol	1145		0.2	DI MS	
14	cis-verbenoi	1145	-	0.3	RI, MS	
15	ClS-	1105	5.5	2.3	KI, MS	
	ol					
16	Borneol	1167		1.5	PL MS	
17	4-Ternineol	1179	0.2	0.9	RI MS	
17		11/)	0.2	0.7	RI, MS	
18	$\alpha$ -Terpineol	1191	-	0.2	KI, MS	
19	Myrtenol	1195	1.6	-	RI, MS	
20	Verbenone	1206	-	0.6	RI, MS	
21	2,4-	1220	-	0.4	RI, MS	
	Dimethylacet					
	ophenone					
22	Carvotanacet	1247	-	0.6	RI, MS	
	one					
23	cis-	1263	31.1	0.4	RI, MS	
	Chrysanthen					
2.1	ylacetate	1071		1.0	<b>DI 1</b> /2	
24	Isopiperiteno	1271	-	1.8	RI, MS	
25	ne	1007	0.0		DI MG	
25	Bornylacetat	1287	0.2	-	KI, MS	
26	e	1216		0.5	DI MS	
20	4- Vinulausiasa	1310	-	0.5	KI, MS	
	v myigualaco					
27	Myrtenylacet	1327	15.1	0.5	RI MS	
27	ate	1527	15.1	0.5	KI, MIS	
28	(Z)-Jasmone	1395	_	0.7	RI MS	
29	B-	1419	-	0.8	RL MS	
	Caryophylle				,	
	ne					
30	2,5-	1424	-	0.3	RI, MS	
	Dimethoxy-					
	<i>p</i> -cymene					
31	α-Humulene	1455	0.7	-	RI, MS	
32	Germacrene	1482	0.8	-	RI, MS	
	D					
33	$\beta$ -Selinene	1487	0.4	0.8	RI, MS	
34	trans-	1492	-	0.2	RI, MS	
	Muurola-					
	4(14),5-					
	diene					
35	epi-Cubebol	1495	-	0.4	RI, MS	
36	Bicyclogerm	1496	0.3	-	RI, MS	

	acrene						
37	α-Muurolene	1499	-	0.5	RI, MS		
38	trans-γ-	1514	-	0.4	RI, MS		
30		1524		2.1	PL MS		
40	Vassana	1524	11.5	2.1	DI MS		
40	Ligulovide	1520	7.4	-	RI, MS		
42	cis-	1553	7.4	0.4	RI MS		
72	Cadineneeth	1555		0.4	KI, WIS		
43	Germacrene D-4-ol	1575	-	1.2	RI, MS		
44	Spathulenol	1577	0.3	-	RI, MS		
45	Caryophylle neoxide	1582	0.3	0.9	RI, MS		
46	Nerylisovale rate	1584	0.2	-	RI, MS		
47	Rosifoliol	1601	0.4	-	RI, MS		
48	Humuleneep oxide II	1607	1.6	0.5	RI, MS		
49	1,10-di- <i>epi</i> - Cubenol	1615	0.8	-	RI, MS		
50	1- <i>epi</i> - Cubenol	1629	-	0.7	RI, MS		
51	T-Cadinol	1641	4.5	3.6	RI, MS		
52	a-Muurolol	1646	-	0.7	RI, MS		
53	$\beta$ -Eudesmol	1650	0.8	0.4	RI, MS		
54	$\alpha$ -Cadinol	1652	-	5.6	RI, MS		
55	Valerianol	1656	3.8	-	RI, MS		
56	14-Hydroxy-	1667	1.1	0.9	RI, MS		
	9- <i>epi-(E)-</i> caryophyllen e						
57	<i>epi-α-</i> Bisabolol	1686	0.4	-	RI, MS		
58	Eudesma- 4(15),7-dien- 1-ol	1688	-	3.5	RI, MS		
59	Bisabolone	1749	2.3	-	RI, MS		
	Total Identification %		97.0	97.3			
	Yields % (w/w)		0.30	0.50			
	Monoterpene hydrocarbon s		5.7	1.4			
	Oxygenated monoterpene s		53.9	55.2			
	Sesquiterpen ehydrocarbo ns		2.2	4.8			
	Oxygenateds esquiterpene s		35.2	18.8			
	Otherderivati ves 17.1						
The main compounds are reported in bold. <sup>a</sup> Order of elution is given on apolarcapillary column DB-5. <sup>b</sup> Retention indices (RI) determined relatively to the retention time of a series of <i>n</i> -alkanes. <sup>c</sup> Relative percentage calculated by GC/FID on an apolar capillary column DB 5. <sup>d</sup> RI: Battinion Logic MS: Mass Sectors in alternative intervent							
DB-5. <sup>a</sup> RI: Retention Indices; MS: Mass Spectra in electronic impact.							

3.2. Electrochemical study

# 3.2.1. Potentiodynamic polarization study

The polarization curve technique was used for the evaluation of the efficiency of the proposed green corrosion inhibitors. The anodic and cathodic polarization curves of the mild steel electrode, at optimal concentrations of different essential oils, in the presence of 1M HCl, at 25 °C are shown in Figure 1.



\*Essential oils: AG: Asteriscus graveolens; PI: Pulicariaincisa.

**Figure 1:** Polarization plots of mild steel in 1M HCl in absence and presence of A.G (0.3 g/L) and P.I (0.3 g/L) after 30 min of immersion and at 25  $^{\circ}$ C

The values of the corrosion potential ( $E_{corr}$ ), cathodic Tafel slope ( $b_c$ ), anodic Tafel slope ( $b_a$ ),  $I_{corr}$ , corrosion rate (CR) and inhibition efficiency (IE (%)) are given in Table 2.

The  $I_{corr}$  and CR values were used to calculate the inhibition efficiency, using the following equations:

$$IE(\%) = \frac{I_{corr}^{\circ} - I_{corr}}{I_{corr}^{\circ}} x 100 \dots \dots (1)$$

where  $I_{corr}^{\circ}$  and  $I_{corr}$  are the corrosion current density values in the absence and presence of inhibitors, respectively, determined by extrapolation of cathodic and anodic Tafel lines to the corrosion potential.

and

$$IE(\%) = \frac{CR_0 - CR}{CR_0} \times 100 \dots \dots (2)$$

where  $CR_0$  and CR are the corrosion rate values in the absence and presence of inhibitors, respectively, determined from polarization curves.

**Table 2:** Electrochemical parameters and the corresponding corrosion inhibition efficiencies for the corrosion of mild steel in 1M HCl containing essential oils at 25  $^{\circ}$ C

	Concent	-E <sub>corr</sub>	-b_	b <sub>a</sub>	Icorr	C.R	EI	EI <sub>C.R</sub>
	ration	(mV/ES	(mV/de	(mV/dec)	(mA/cm <sup>2</sup> )	(mm/Y)	Icorr(%)	(%)
	(g/L)	<b>C</b> )	<u>c</u> )					
Blank		456	131	137	2.93	34.28		
$A.G^*$	0.1	456	134	108	0.83	9.77	71.67	71.50
	0.3	442	160	80	0.42	4.9	85.66	85.70
$P.I^*$	0.1	460	98	132	0.69	8.023	76.45	76.40
	0.19	445	68	160	0.383	4.48	86.93	86.93
	0.3	441	70	202	0.38	4.45	87.03	87.02

#### \* Essential oils: AG: Asteriscusgraveolens; PI: Pulicariaincisa

From the examination of Table 2, it is possible to deduce that after adding these green inhibitors to 1M HCl, both anodic and cathodic corrosion reactions of mild steel electrode were inhibited. This inhibition is increased by increasing the inhibitor concentration from 0.1 to 0.3g/L

Chaib et al., 2020

(optimal concentration) and achieves an efficiency of 85.66% and 87.03% for A. graveolens and P. incisa, respectively. This behavior indicates that the addition of the inhibitors delays the reduction of hydrogen ions at the cathode and also reduces the dissolution reaction at the anode (mild steel) [1-2, 23]. The molecules of essential oil can be classified as a mixed-type inhibitor because the values of corrosion potential of mild steel in the acidic solution in the presence of inhibitor change slightly compared to the corrosion potential in the presence of the acid alone. The addition of the two green inhibitors to the corrosive medium leads to a decrease in corrosion current densities of mild steel [3, 24-26]. From Table 2, it can easily be observed that the corrosion rates (CR) decrease considerably in the presence of the different essential oils obtained from the studied plants.

#### 3.2.2. Linear polarization technique

Linear polarization technique was performed in 1M HCl with different concentrations of the two essential oils. The corresponding polarization resistance  $(R_p)$  values are given in Table 3.

**Table 3:** Polarization resistance and inhibition efficiency forthe corrosion of mild steel in 1M HCl containing essentialoils at 25 °C

	Concentration (g/L)	Rp	EI <sub>Rp</sub> (%)			
Blanc		8.62				
$A.G^*$	0.1	27.84	69.04			
	0.3	43.90	80.36			
P.I*	0.1	30.27	71.52			
	0.19	45.10	81.55			
0.3 48.03 82.05						
*Essential oils: AG: Asteriscus graveolens; PI:						
Pulicaria incise						

The inhibition efficiency of corrosion of mild steel is calculated by polarization resistance as follows:

$$IE(\%) = \frac{R_p - R_p^0}{R_p} \times 100 \dots \dots (3)$$

where  $R_p$  and  $R_P^0$  are the polarization resistance values with and without inhibitors, respectively.

It is apparent that  $R_p$  and inhibition percentage (IE%) increase with increasing inhibitor concentration. The values of IE% attain 80.36 and 82.05% at 0.3 g/L (optimal concentration) for *A. graveolens* and *P. incisa*, respectively. Therefore, these results indicate that the inhibiting action of the two essential oils is satisfactory. Furthermore, the inhibition efficiencies obtained both by potentiodynamic polarization and by polarization resistance methods are in good agreement.

#### 3.2.3. Electrochemical impedance spectroscopy (EIS)

The corrosion behaviour of mild steel in 1M HCl in the absence and the presence of two essential oils of for *A*. *graveolens* and *P*. *incisa*, after 30 min of immersion and at 25°C. A typical set of Nyquist plots for mild steel in uninhibited and inhibited 1M HCl is shown in Figs. 2 that exhibit one semicircle, which centre lies under the abscissa.



Essential oils: AG: Asteriscus graveolens; PI: Pulicari aincisa

**Figure 2:** Nyquist plots for the mild steel in 1M HCl in the absence and presence of A.G (0.3 g/L) and P.I (0.3 g/L) after 30 min of immersion and at 25 °C

The appearance of one semicircle in the impedance diagrams was common to most of these compounds To describe the observed depression of the capacitive semicircle it is necessary to replace the capacitor by some element, which has frequency dispersion like the constant phase element (CPE) [27-29]. The dispersion of the capacitive semicircle is explained also by surface heterogeneity due to surface roughness, impurities or dislocations, distribution of activity centres, inhibitors adsorption and formation of porous layers [28].

The impedance of the CPE is [29]:

$$\mathbf{Z}_{\text{CPE}} = \mathbf{Q}^{-1} (\mathbf{j}\boldsymbol{\omega})^{-n} \dots \dots \dots (4)$$

where Q is a proportionality coefficient and n an exponent related to the phase shift. For whole numbers of n = 1, 0, -1, CPE is reduced to the classical lumped elements capacitor (C), resistance (R) and inductance (L), respectively. The value of n = 0.5 corresponds to Warburg impedance (W). Values of n can serve as a measure of the surface heterogeneity. The equivalent circuit model employed for these systems is presented in Figure 3.



Figure 3: The equivalent circuit of the impedance spectra obtained

The resistance  $R_s$  is the resistance of the solution;  $R_t$  reflects the charge transfer resistance and CPE has the meaning of a frequency distributed double-layer capacitance. The curves of the obtained plots were approximated by single capacitive semicircles. This phenomenon indicates that the corrosion process was mainly charge-transfer controlled [23-24]. The corresponding electrochemical parameters extracted from these plots are presented in Table 4, where it can be observed that by increasing the concentration of inhibitor, the R<sub>ct</sub> values increases (and hence IE % increases), while the C<sub>dl</sub> values decreases. The higher values of R<sub>ct</sub> are attributable to a slower rate of corrosion of mild steel. The decrease in the values of C<sub>dl</sub> might result from the lowering of general dielectric constant or from the increase in thickness of the electrical double layer, which suggests the adsorption of inhibitor molecules on mild steel surface [25-27].

Note that the capacitances were calculated from Q and  $R_t$  using the equation [28-29]:

$$\mathbf{Q} = \frac{(\mathbf{CR}_t)^n}{\mathbf{R}_t} \dots \dots \dots (5)$$

**Table 4:** Impedance parameters and inhibition efficiency for

 the corrosion of mild steel in 1 M HCl containing different

 inhibitors

	Conc. (g/L)	$\begin{array}{c} \mathbf{Q} \\ (\mathbf{\Omega}^{-1}.\mathbf{cm}^{-1}.\mathbf{cm}^{-1}.\mathbf{s}^{n}) \end{array}$	n	$R_t$ ( $\Omega$ cm <sup>2</sup> )	C <sub>dl</sub> (μF cm <sup>-2</sup> )	EI <sub>Rt</sub> (%)
Blank		3.76x10 <sup>-4</sup>	0.86	6.92	865.06	
A.G*	0.1	2.15x10 <sup>-4</sup>	0.87	17.77	448.33	61.06
	0.3	1.49x10 <sup>-4</sup>	0.87	26.90	305.35	74.27
P.I*	0.1	1.69x10 <sup>-4</sup>	0.86	21.19	369.72	67.34
	0.19	1.29x10 <sup>-4</sup>	0.87	32.81	266.84	78.90
	0.3	1.07x10 <sup>-4</sup>	0.88	39.34	209.70	82.41

Essential oils: AG: Asteriscus graveolens; PI: Pulicari aincisa

#### 3.2.4. Adsorption consideration

The corrosion inhibition can be referred to the adsorption on the metal surface of the main components and/or other molecules present in the essential oils of the two plants (A.G and P.I). For the commodity, we have only studied the adsorption of *P. incisa*. The adsorption of these compounds on the mild steel surface reduces the surface area available for corrosion. The values of surface coverage ( $\theta$ =I.E%/100) for different concentrations of the essential oils of *P. incise* can be obtained from polarization curves measurements.

The surface coverage values ( $\theta$ ) were tested graphically to allow fitting of a suitable adsorption isotherm.

The plot of C/ $\theta$  versus C (Fig.3) yielded straight lines with slopes equal to 1.12, clearly proving that the adsorption of the molecules inhibitors from 1M HCl solution on the mild steel obeys the modified Langmuir adsorption isotherm where,

with

$$K_{ads} = \frac{1}{55.5} \exp\left(\frac{\Delta G_{ads}}{RT}\right)$$

 $\frac{C}{\theta} = \frac{n}{K_{ads}} + nC \dots \dots (4)$ 

Where  $K_{ads}$  is the equilibrium constant for the adsorption process, C is the concentration of the inhibitor and  $\theta$  is the surface coverage.

The values of equilibrium adsorption constant obtained from this isotherm are about 157. The largest negative values of  $\Delta G_{ads}$ , i.e. -22.48 kJ/mol, indicate that this extract oil is strongly adsorbed onto the mild steel surface.



**Figure 3:** Langmuir adsorption isotherm for steel in 1M HCl with *P. incisa* oil

# 3.2.5. Inhibition mechanism

It is known that the inhibitory effect against corrosion by an essential oil is the adsorption of its phytochemical constituents on the mild steel surface [30]. In addition and because of the complex chemical composition of an essential oil, the inhibitory effect cannot be attributed to a particular constituent. This difficulty of attribution is due to the fact that some of these substances contain different functional groups, such as oxide, esters and alcohols ones [8]. Moreover, these compounds contain oxygen atoms in the functional groups (C=O, C-O, O-H), often together with aromatic rings, which contain  $\pi$  electrons in their structure. This allows them to have the characteristics of good corrosion inhibitors [12, 31]. It should be noted that the essential oils used in this study contain several constituents having the above characteristics, for example in the oil of A. graveolens, cis-chrysanthenyl acetate, kessane, liguloxide and other minor components are present. On the other hand, the high inhibition efficiency of the essential oil *P. incisa* is attributable to the fact that more than 50% of the composition of this oil is constituted by two products: 2,6-dimethylphenol (12.6%) and chrysanthenone (45.3%).



However, together with these two main compounds, also other minor components might be involved in some type of synergism effect.

## 4. Conclusions

The current study indicates that the hydro-distilled oils of A. graveolens and P. incisa, two Asteraceae from southern Algeria, were constituted in majority by terpenoids. In the case of A. graveolens, the principal components were cis-chrysanthenyl acetate, myrtenyl acetate, kessane, liguloxide and cis-chrysanthenol; whereas in P. incisa oil the main constituent was chrysanthenone. These essential oils show good inhibition properties on the corrosion of mild steel in 1M HCl medium at 25°C. The inhibition efficiency increases with increasing oils concentrations. The values of the inhibition efficiencies estimated from electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization measurement were in good agreement. By analyzing polarization results, the oils, being rich in oxygenated components, mainly act as a mixed-type inhibitor, with predominant cathodic effectiveness. Adsorption of P. incise oil on the mild steel in 1M HCl obeys the Langmuir adsorption isotherm model. It should be noted that the addition of P. incisa oil leads to an increase in activation corrosion energy, indicating that the inhibitor is strongly adsorbed on the metal surface.

#### Funding

This research was financially supported by Abou Bekr Belkaïd University–Tlemcen and the Ministry of Higher Education and Scientific Research of the Algerian People's Democratic Republic under the project PRFU (Ref. B00L01UN130120180009).

# Acknowledgements

The authors are grateful to Dr Rabéa Sahki of the National Forest Research Institute, Tamanrasset (Algeria), for the taxonomic identification of the Asteraceae studied.

# Author contribution statement

Author Contributions: A.H. designed research; C.F., A.H., B.O. and F.G. performed the research and analyzed the data; A.H. and B.O. wrote the paper. All authors read and approved the final manuscript.

# Conflict of interest

The authors declare that there are no conflicts of interest.

# References

- [1] O. Benali, L. Larabi, S. Merah, Y. Harek, Influence of the Methylene Blue Dye (MBD) on the corrosion inhibition of mild steel in 0.5 M sulphuric acid, Part I: weight loss and electrochemical studies, J. Mater. Environ. Sci., 2 (2011) 39-48.
- [2] O. Benali, M. Ouazene, Inhibition of cold rolled steel corrosion in sulphuric acid solution by 2mercapto-1-methylimidazole: Time and temperature effects treatments, Arab. J. Chem., 4 (2011) 443-448.
- [3] H.B. Ouici, M. Tourabi, O. Benali, C. Selles, C. Jama, A. Zarrouk, F. Bentiss, Adsorption and corrosion inhibition properties of 5-amino 1,3,4-thiadiazole-2-thiol on the mild steel in hydrochloric acid medium: Thermodynamic, surface and electrochemical studies, J. Electroanal. Chem., 803 (2017) 125-134.
- [4] H.T. Rahal, M. Abdel-Gaber, G.O. Younes, Inhibition of steel corrosion in nitric acid by sulfur containing compounds, Chem. Eng. Commun., 203(4) (2016) 435-445.
- [5] M. Boudalia, A. Guenbour, A. Bellaouchou, A. Laqhaili, M. Mousaddak, A. Hakiki, B. Hammouti, E.E. Ebenso, Corrosion inhibition of organic oil extract of leaves of L. stoekas on stainless steel in concentrated phosphoric acid solution, Int. J. Electrochem. Sci., 8 (2013) 7414-7424.
- [6] M. Abdulwahab, O.S.I. Fayomi, A.P.I. Popoola, F. Asuke, L.E. Umoru, Effect of Avogadro natural oil on the corrosion inhibition of mild steel in hydrochloric acid solution, Res. Chem. Intermed., 40: (2014) 1115-1123.
- [7] L. Afia, R. Salghi, L. Bammou, El. Bazzi, B. Hammouti, L. Bazzi, A. Bouyanzer, Anti-corrosive properties of Argan oil on C38 steel in molar HCl solution, J. Saudi Chem. Soc., 18 (2014) 19-25.
- [8] L. Afia, O. Benali, R. Salghi, E.E. Ebenso, S. Jodeh, M. Zougagh, B. Hammouti, Steel corrosion inhibition by acid garlic essential oil as a green

corrosion inhibitor and sorption behavior, Int. J. Electrochem. Sci., 9 (2014) 8392-8406.

- [9] D. Benhamamou, R. Salghi, Lh. Bazzi, B. Hammouti, S.S. Al-Deyab, L. Bammou, L. Bazzi, A. Bouyanzer, Prickly pear seed oil extract: a novel green inhibitor for mild steel corrosion in 1M HCl solution, Int. J. Electrochem. Sci., 7 (2012) 1303-1318.
- [10] K. Boumhara, M. Tabyaoui, C. Jama, F. Bentiss, Artemisia mesatlantica essential oil as green inhibitor for carbon steel corrosion in 1M HCl solution: electrochemical and XPS investigations, J. Ind. Eng. Chem. 29 (2015) 146-155.
- [11] M. Znini, J. Paolini, L. Majidi, J-M. Desjobert, J. Costa, N. Lahhit, A. Bouyanzer Evaluation of the inhibitive effect of essential oil of L. multifda L. on the corrosion behavior of C38 steel in 0.5M H<sub>2</sub>SO<sub>4</sub> medium, Res. Chem. Intermed., 38 (2) (2012) 669-683.
- [12] M. Znini, G. Cristofari, L. Majidi, A. Ansari, A. Bouyanzer, J. Paolini, J. Costa, B. Hammouti Green approach to corrosion inhibition of mild steel by essential oil leaves of Asteriscus graveolens (Forssk.) in sulphuric acid medium, Int. J. Electrochem. Sci., 7 (2012) 3959-3981.
- [13]S. Archana, S. Anurag, S. Deepti, J. Praveen, Corrosion inhibition and adsorption behavior of clove oil on iron in acidic medium, J. Chem. 9 (2012) 2044-2051.
- [14] O. Mokhtari, I. Hamdani, A. Chetouani, A. Lahrach, H. El Halouani, A. Aouniti, M. Berrabah, Inhibition of steel corrosion in 1M HCl by Jatrophacurcas oil, J. Mater. Environ. Sci., 5(1) (2014) 310-319.
- [15] M. Znini, M. Bouklah, L. Majidi, S. Kharchouf, A. Aouniti, A. Bouyanzer, B. Hammouti, J. Costa, S.S. Al-Deyab, Chemical composition and inhibitory effect of Mentha spicata essential oil on the corrosion of steel in molar hydrochloric acid, Int. J. Electrochem. Sci., 6 (2011) 691–704.
- [16] S. Vadivu, R. Saratha, R. Vasantha Jothi, Corrosion inhibition of mild steel in hydrochloric acid medium using plant extracts–a succinct review, Inter. J. Sci. Eng. Tech. Res., 5(12) (2016) 3324-3340.
- [17] W. Greuter, Save Asteriscus, sink Nauplius (Compositae), Flore Mediterranea, 7 (1997) 41-48.
- [18] A. Sahki, R. Sahki Le Hoggar-Promenade Botanique, Esope, Lyon/Chamonix, (2004) p. 1-311.
- [19] European Pharmacopoeia, Council of Europe, 5<sup>th</sup> Ed., Volume I, Strasbourg Cedex, France, (2004) p. 217-218.
- [20] F. Chaib, H. Allali, M. Bennaceur, G. Flamini, Chemical composition and antimicrobial activity of essential oils from the aerial parts of Asteriscus graveolens (FORSSK.) LESS. And Pulicar iaincisa (LAM.) DC.: Two Asteraceae herbs growing wild in the Hoggar, Chem. Biodiv., 14 (2017).
- [21] E. A. Shahat, R. O. Bakr, O. A. Eldahshan, N.A. Ayoub, Chemical composition and biological activities of the essential oil from leaves and flowers

of Pulicariaincisa sub. candolleana growing in Egypt, Chem. Biodiv., 14 (2017).

- [22] O. Benali, L. Larabi, B. Tabti, Y. Harek, Influence of 1-methyl 2-mercapto imidazole on corrosion inhibition of carbon steel in 0.5 M H<sub>2</sub>SO<sub>4</sub>, Anti-Corros. Meth. Mater., 52(5) (2005) 280-285.
- [23] H.B. Ouici, O. Benali, Y. Harek, L. Larabi, B. Hammouti, A. Guendouzi, Inhibition of mild steel corrosion in 5 % HCl solution by 5-(2hydroxyphenyl)-1,2,4-triazole-3-thione, Res. Chem. Intermed. 39 (2013) 2777-2793.
- [24] H.B. Ouici, O. Benali, Y. Harek, L. Larabi, B. Hammouti, A. Guendouzi, The effect of some triazole derivatives as inhibitors for the corrosion of mild steel in 5% hydrochloric acid, Res. Chem. Intermed. 39 (2013) 3089-3103.
- [25] H.B. Ouici, M. Tourabi, O. Benali, C. Selles, M. Traisnel, C. Jama, F. Bentiss R. Salghi, Experimental investigation on the corrosion inhibition characteristics of mild steel by 5-(2hydroxyphenyl)-1,3,4-oxadiazole-2-thiol in hydrochloric acid medium, J. Mater. Environ. Sci., 7 (2016) 2971-2988.
- [26] O. Benali, L. Larabi, S.M. Mekelleche, Y. Harek, Influence of substitution of phenyl group by

naphthyl in a diphenyl thiourea molecule on corrosion inhibition of cold-rolled steel in 0.5 M  $H_2SO_4$ , J. Mater. Sci. 41 (2006) 7064-7073.

- [27] F. Boudjellal, H.B. Ouici, A. Guendouzi, O. Benali, A Sehmi Experimental and theoretical approach to the corrosion inhibition of mild steel in acid medium by a newly synthesized pyrazole carbothioamide heterocycle, J. Mol. Struc., 1199 (2020) 127051.
- [28] S. Messikh, R. Salhi, O. Benali, H. B. Ouici, N. Gherraf, Synthesis and evaluation of 5-(Phenyl)-4H-1,2,4-triazole-3-thiol as Corrosion Inhibitor for Mild Steel in 0.5M H<sub>2</sub>SO<sub>4</sub> and its synergistic effect with potassium iodide, Inter. J. Chem. Biochem. Sci., 17 (2020) 14-38.
- [29] S. Andreani, M. Znini, J. Paolini, L. Majidi, B. Hammouti, J. Costa, A. Muselli, Study of corrosion inhibition for mild steel in hydrochloric acid solution by Limbardacrithmoides (L.) essential oil of Corsica. J. Mater. Environ. Sci. 7(1) (2016) 187-195.
- [30] H.E. Megahed, M. Sobhi, S. Nour Celery (Apium graveolens) extract as corrosion inhibitor for carbon steel in 1 M HCl, J. Basic. Environ. Sci., 4 (2017) 170-17.